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(54) **Crystalline aluminophosphates and related compounds.**

(57) The present invention relates to crystalline aluminophosphates and related compounds having in the as-synthesized anhydrous form an X-ray diffraction pattern containing at least the lines given in Table A.

TABLE A

d (Å)	Intensity (I/I_0)
17.5 ± 0.2	vs
8.45 ± 0.2	s/vs
5.35 ± 0.1	w/m
4.62 ± 0.1	w/m
3.70 ± 0.05	w/m
3.52 ± 0.03	m
3.41 ± 0.03	m/s

The invention further relates to a process for preparing the crystalline aluminophosphates and related compounds, using a substituted diamine as an organic template, under specified reaction conditions. The invention further relates to the use of the crystalline aluminophosphates and related compounds in separation processes and processes involving catalytic reactions.

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The present invention relates to crystalline aluminophosphates and related compounds, a process for preparing such crystalline aluminophosphates and related compounds and the use of crystalline aluminophosphates and related compounds in catalytic processes as well as separation processes.

Crystalline aluminophosphates and related compounds are well known materials which find a promising reception in industry as new generations of molecular sieves, catalyst carriers as well as catalysts.

Compounds related to aluminophosphates include crystalline compounds in the $SAPO_4$ - (siliconaluminophosphate), $MeAPO_4$ (metalloaluminophosphate) and $ElAPO_4$ (non-metal substituted aluminophosphate) families.

In European patent specification No. 43 562 the preparation of various crystalline aluminophosphates and related compounds is described from starting mixtures containing inter alia organic structure directing or templating agents. In Example 51 of said patent specification it is described that an aluminophosphate, designated $AlPO_4$-21, can be prepared by keeping a starting mixture, comprising N,N,N',N'-tetramethyl ethylene diamine, at a temperature of 200 °C for 168 hours.

It has now been found that novel crystalline aluminophosphates and related compounds, for example of the $SAPO_4$ and $MeAPO_4$-type, may be prepared from starting mixtures when use is made of the appropriate forming components, the required forming conditions and a source of a diamine as organic template.

The present invention thus relates to novel crystalline aluminophosphates and related compounds having in the as-synthesized anhydrous form an X-ray diffraction pattern containing at least the lines given in table A.

TABLE A

d (Å)	Intensity (I/I_0)
17.5 ± 0.2	vs
8.45 ± 0.2	s/vs
5.35 ± 0.1	w/m
4.62 ± 0.1	w/m
3.70 ± 0.05	w/m
3.52 ± 0.03	m
3.41 ± 0.03	m/s
(v)w = (very) weak, m = moderate, (v)s = (very) strong d (A) = d_{hkl} spacing in Angstrom (10^{-10} m). Intensity (I/I_0) = intensity of peaks in X-ray diffraction pattern relative to the strongest peak.	

In particular, the present invention relates to novel crystalline aluminophosphates and related compounds having in the as-synthesized anhydrous form an X-ray diffraction pattern containing at least the lines given in table I.

TABLE I

d (Å)	Intensity (I/I_0)
17.5 ± 0.2	vs
8.7 ± 0.2	w/m
8.45 ± 0.2	s/vs
5.35 ± 0.1	w/m
4.62 ± 0.1	w/m
4.41 ± 0.05	w
4.26 ± 0.05	m
3.98 ± 0.05	m
3.70 ± 0.05	w/m
3.52 ± 0.03	m
3.41 ± 0.03	m/s
2.91 ± 0.03	w/m

Crystalline aluminophosphates and related compounds of the present invention are further characterized in that they have in the as-synthesized anhydrous form a chemical composition $mR(X_nY_rAl_qP_x)O_2$, wherein R represents a diamine of the general formula $R_2R_3N\text{-}R_1\text{-}NR_4R_5$, wherein R_1 represents a C_2 carbon chain which may contain one or more inert substituents and each of R_2, R_3, R_4 and R_5 represents a hydrogen atom or a methyl or ethyl group which methyl or ethyl group may contain one or more inert substituents, and wherein $R_2 + R_3 + R_4 + R_5$ comprise at least two of methyl and/or ethyl groups, X represents one or more elements which may substitute for P, Y represents one or more elements which may substitute for Al, wherein

$m = 0.03 - 0.2$
$n = 0 - 0.4$
$r = 0 - 0.4$
$q = 0.3 - 0.6$
$x = 0.3 - 0.6$
and wherein $n + r + q + x = 1$.

In the event that $n > 0$ and/or $r > 0$, it will be appreciated that the as-synthesized anhydrous form also contains an appropiate charge-balancing cation, such as a proton or a protonated form of the organic template R.

It should be understood that the as-synthesized anhydrous form referred to in this specification may also contain chemically bound water as the case may be.

Although the elements denoted X have a preference for substituting P, and the elements denoted Y have a preference for substituting Al, it is to be noted that some of the elements X and Y may substitute the non-preferred elements Al and P respectively. This is especially true for elements denoted X.

Preferably, crystalline aluminophosphates and related compounds of the present invention are characterized in that they have, in the as-synthesised anhydrous form, a chemical composition wherein

$m = 0.05 - 0.15$
$n = 0 - 0.4$
$r = 0 - 0.2$
$q = 0.3 - 0.6$ and
$x = 0.3 - 0.6$.

Typically, X represents one or more tetra- or pentavalent elements. Preferably, X represents one or more elements chosen from the group of Si, Ge, As and V. More preferably, X represents one or more elements chosen from the group of V and Si.

Typically, Y represents one or more di- or trivalent elements. Preferably, Y represents one or more elements chosen from the group of Mg, Co, Mn, Zn, Fe, Ni, Cr and Ga. More preferably, Y represents one or more elements chosen from the group of Co and Mg.

Typically, R represents an ethylene diamine of the general formula $R_2R_3N\text{-}CH_2\text{-}CH_2\text{-}NR_4R_5$, wherein each of R_2, R_3, R_4 and R_5 represents a methyl or ethyl group. Preferably, R represents N,N,N',N'-tetramethyl ethylene diamine.

The invention also relates to crystalline aluminophosphates and related compounds, having in the substantially R-free form the general chemical composition $(X_nY_rAl_qP_x)O_2$, wherein X, Y, n, r, q and x have the meaning as described hereinabove, and wherein $n + r + q + x = 1$.

The invention further relates to a process for preparing crystalline aluminophosphates and related compounds from a starting mixture comprising a source of aluminium, a source of phosphorus, a source of a diamine as defined hereinbefore, and optionally a source of a component X and/or Y, keeping the starting mixture at a temperature of from 100 to 170 °C for a synthesis time sufficient to form crystalline aluminophosphate or related compound followed by separating off the crystalline aluminophosphate or related compound and drying, in which starting mixture the various components are initially present in the following molar ratios:

$R : (Al + P + X + Y) = 0.1 - 0.3$
$X : Al = 0 - 1$
$Y : Al = 0 - 1$
$P : Al = 0.5 - 2$
$H_2O : Al = 5 - 500$,

wherein R, X and Y have the meanings as defined hereinbefore.

Preferably, a starting mixture is used wherein the various components are initially present in the following molar ratios:

$R : (Al + P + X + Y) = 0.15 - 0.25$
$X : Al = 0 - 0.5$
$Y : Al = 0 - 0.4$
$P : Al = 0.6 - 1.6$
$H_2O : Al = 10 - 100$.

Preferably, the synthesis time is kept in the range of from 10 to 150 hours, more preferably of from 10 to 120 hours.

The process is preferably carried out by keeping the starting mixture at a temperature of from 110 to 160 °C, more preferably of from 130 to 160 °C.

It will be understood that at relatively low starting mixture temperatures the synthesis time will be rather long and vice versa. It will be understood that the optimal process conditions can be chosen within the ranges as mentioned hereinabove. Higher temperatures and/or longer synthesis times than those envisaged in the process according to the present invention will result in the formation of unwanted products such as $AlPO_4$-21.

For preparing the starting mixture, any source or promoter form based on a diamine as defined hereinbefore can be used as a template and/or structure directing agent, such as a quaternary ammonium compound of such diamine, which source or promoter should be such that it can be converted into the appropriate diamine.

The process according to the present invention may be carried out at autogeneous pressure as well as at elevated pressure.

Examples of suitable aluminium sources comprise aluminium salts, aluminium (hydr)oxides, such as gamma and theta alumina, gibbsite, boehmite, pseudo-boehmite and aluminium alkoxides, such as aluminium triisopropoxide and mixtures of various aluminium sources. Typically, boehmite or pseudo-boehmite is used as an alumina source.

Examples of suitable phosphorus sources comprise phosphorus acids and derivates thereof such as esters, phosphorus oxides, phosphates and phosphites and mixtures of various phosphorus sources. Typically, phosphoric acids are used as a phosphorus source.

Examples of suitable sources of X and/or Y comprise the appropriate chlorides, iodides, bromides, nitrates, sulphates, oxides, hydroxides, alkoxides and acetates, preferably acetates, alkoxides and/or oxides.

It has been found that agitation during crystallisation can be applied advantageously to produce the desired crystalline aluminophosphates and related compounds from the starting mixture. In order to facilitate crystallisation, it may be desired to add seeds to the starting mixture.

If desired, the organic template R may be removed substantially by thermal treatment and/or by suitable wet chemical oxidation reactions means, such as a hydrogen peroxide treatment, to obtain crystalline aluminophosphates and related compounds substantially free of organic template R.

The crystalline aluminophosphates and related compounds according to the present invention may be used as molecular sieves, catalysts or as catalyst carriers in the operation of various catalytic processes. If desired, one or more (catalytically) active species, in particular protons and/or precursors thereof and/or one or more metal(s) compounds of Group I, II, III and/or the Transition Metals and/or Rare Earth metals and/or precursors thereof, can be introduced into the crystalline aluminophosphates and related compounds according to the present invention.

They can be introduced by well known techniques such as, for instance, impregnation and ion-exchange.

Alternatively, the crystalline aluminophosphates or related compounds of the present invention may be used as molecular sieves in separation processes.

The invention will now be illustrated by means of the following Examples.

Example I

A crystalline $AlPO_4$, referred to as SCS-24, was prepared by mixing 9.3 grammes of pseudoboehmite (Catapal B) as alumina source, 15.4 grammes of 85% ortho-phosphoric acid, 7.7 grammes of N,N,N',N'-tetramethyl ethylene diamine and 45.6 grammes of water, giving a starting mixture composition on a molar basis of 1 Al_2O_3 : 1 P_2O_5 : 1 R : 45 H_2O. After homogenation, the starting mixture was transferred to a rotating teflon-lined autoclave where it was kept at 140 °C under autogeneous pressure for a period of 72 hours.

After synthesis, the crystalline compound produced was separated from the mother liquor by centrifugation, water washed and dried.

The crystalline compound obtained, had in the anhydrous form the chemical composition 0.11 R $(Al_{0.5}P_{0.5})O_2$ and an X-ray diffraction pattern containing the lines given in Table II.

TABLE II

d (Å)	Intensity (I/I_o)
17.55	100
8.70	45
8.44	85
6.18	14
5.504	25
5.347	21
4.620	19
4.408	10
4.255	52
3.977	49
3.698	40
3.515	47
3.409	60
2.906	20
2.875	20

Examples II to V

The experiment described in Example I was repeated but applying the synthesis temperatures and times as indicated in Table III.

Table III

Example	Synthesis Time [h]	Synthesis Temp. [°C]	Product XRD
II	72	130	SCS-24
III	72	150	SCS-24
IV	24	160	SCS-24
V	72	180	$AlPO_4$-21

The experiments described in Examples II, III and IV yielded SCS-24 having essentially the same lines in its X-ray diffraction pattern as shown in Table II. The comparative experiment described in Example V yielded $AlPO_4$-21. It can be seen that at synthesis temperatures and times lying within the scope of the present invention, a product (SCS-24) in accordance with the present invention is obtained. For example, at a synthesis temperature of 160 °C and a synthesis time of 24 hours a beautiful crystalline SCS-24 is obtained. However, as shown in Example V, at a synthesis temperature outside the range as claimed in the present invention $AlPO_4$-21 is obtained.

Example VI

The experiment described in Example I was repeated but using a starting mixture composition on a molar basis of 0.8 Al_2O_3 : 1 P_2O_5 : 1 R : 45 H_2O. After working up (synthesis, separation, washing, drying) SCS-24 was obtained having essentially the same lines in its X-ray diffraction pattern as shown in Table II.

Example VII

The experiment described in Example I was repeated but using a starting mixture composition on a molar basis of 1 Al_2O_3 : 1 P_2O_5 : 0.5 R : 45 H_2O and applying a synthesis temperature of 120 °C. After working up SCS-24 was obtained together with a substantial amount of an aluminophosphate having the tridymite crystal structure, the former having essentially the same lines in its X-ray diffraction pattern as shown in Table II.

Example VIII

A crystalline $CoAPO_4$ was prepared by repeating the experiment described in Example I but with the addition of cobalt acetate tetrahydrate, to yield a starting mixture composition on a molar basis of 0.15 CoO : 1 Al_2O_3 : 1 P_2O_5 : 1 R : 45 H_2O.

The crystalline compound obtained, had in the anhydrous form the chemical composition 0.10 R $(Co_{0.03}Al_{0.47}P_{0.5})O_2$ and an X-ray diffraction pattern containing essentially the same lines as given in Table II.

Example IX

A crystalline $SAPO_4$ was prepared by repeating the experiment described in Example I but with the addition of silica gel to yield a starting mixture composition on a molar basis of 0.5 SiO_2 : 1 Al_2O_3 : 1 P_2O_5 : 1 R : 45 H_2O.

The crystalline compound obtained, had in the anhydrous form the chemical composition 0.11 R $(Si_{0.13}Al_{0.45}P_{0.42})O_2$ and an X-ray diffraction pattern containing essentially the same lines as given in Table II.

Example X

A crystalline $SAPO_4$ was prepared by repeating the experiment described in Example I but with the addition of tetraethyl orthosilicate to yield a starting mixture composition on a molar basis of 0.5 SiO_2 : 1 Al_2O_3 : 1 P_2O_5 : 1 R : 45 H_2O.

The crystalline compound obtained, had in the anhydrous form the chemical composition 0.12 R $(Si_{0.05}Al_{0.47}P_{0.48})O_2$ and an X-ray diffraction pattern containing essentially the same lines as given in Table II.

Claims

1. Crystalline aluminophosphates and related compounds having in the as-synthesized anhydrous form an X-ray diffraction pattern containing at least the lines given in table A.

2. Crystalline aluminophosphates and related compounds as claimed in claim 1, having in the as-synthesized anhydrous form an X-ray diffraction pattern containing at least the lines given in table I.

3. Crystalline aluminophosphates and related compounds as claimed in claim 1 or 2, having in the as-synthesized anhydrous form the chemical composition $mR(X_nY_rAl_qP_x)O_2$, wherein R represents a diamine of the general formula $R_2R_3N\text{-}R_1\text{-}NR_4R_5$, wherein R_1 represents a C_2 carbon chain which may contain one or more inert subtsituents and each of R_2, R_3, R_4 and R_5 represents a hydrogen atom or a methyl or ethyl group which methyl or ethyl group may contain one or more inert substituents, and wherein $R_2 + R_3 + R_4 + R_5$ comprise at least two of methyl and/or ethyl groups, X represents one or more elements which may substitute for P, Y represents one or more elements which may substitute for Al, wherein
   m = 0.03 - 0.2
   n = 0 - 0.4
   r = 0 - 0.4
   q = 0.3 - 0.6
   x = 0.3 - 0.6
   and wherein $n + r + q + x = 1$.

4. Crystalline aluminophosphates and related compounds as claimed in claim 3, wherein
   m = 0.05 - 0.15
   n = 0 - 0.4

r = 0 - 0.2
q = 0.3 - 0.6 and
x = 0.3 - 0.6.

5. Crystalline aluminophosphates and related compounds as claimed in any one of claims 3 or 4, wherein X represents one or more tetra- or pentavalent elements, preferably represents one or more elements chosen from the group of V, Ge, As and Si, more preferably represents one or more elements chosen from the group of V and Si.

6. Crystalline aluminophosphates and related compounds as claimed in any one of claims 3-5, wherein Y represents one or more di- or trivalent elements, preferably represents one or more elements chosen from the group of Mg, Co, Mn, Zn, Fe, Ni, Cr and Ga, more preferably represents one or more elements chosen from the group of Co and Mg.

7. Crystalline aluminophosphates and related compounds as claimed in any one of claims 3-6, wherein R represents an ethylene diamine of the general formula $R_2R_3N\text{-}CH_2\text{-}CH_2\text{-}NR_4R_5$, wherein each of R_2, R_3, R_4 and R_5 represents a methyl or ethyl group, preferably R represents N,N,N',N'-tetramethyl ethylene diamine.

8. Crystalline aluminophosphates and related compounds according to any one of claims 1-7, whenever obtained in a substantially R-free form.

9. Crystalline aluminophosphates and related compounds as claimed in any preceding claim, wherein one or more (catalytically) active species have been introduced, in particular protons and/or precursors thereof and/or one or more metal(s) compounds of Group I, II, III and/or the Transition Metals and/or Rare Earth metals and/or precursors thereof.

10. Process for preparing crystalline aluminophosphates and related compounds as claimed in claim 1, from a starting mixture comprising a source of aluminium, a source of phosphorus, a source of a diamine as defined hereinbefore, and optionally a source of a component X and/or Y, keeping the starting mixture at a temperature of from 100 to 170 °C for a synthesis time sufficient to form a crystalline aluminophosphate or related compound followed by separating off the crystalline aluminophosphate or related compound obtained and drying, in which starting mixture the various components are initially present in the following molar ratios:

R : (Al + P + X + Y) = 0.1 - 0.3
X : Al = 0 - 1
Y : Al = 0 - 1
P : Al = 0.5 - 2 and
H_2O : Al = 5 - 500.

11. Process as claimed in claim 10, wherein the starting mixture the various components are initially present in the following molar ratios:

R : (Al + P + X + Y) = 0.15 - 0.25
X : Al = 0 - 0.5
Y : Al = 0 - 0.4
P : Al = 0.6 - 1.6
H_2O : Al = 10 - 100

12. Process as claimed in claim 10 or 11, wherein the synthesis time is kept in the range of from 10 to 150 hours, preferably in the range of from 10 to 120 hours.

13. Process as claimed in any one of claims 10-12, wherein the starting mixture is kept at a temperature of from 110 to 160 °C, preferably of from 130 to 160 °C.

14. Process as claimed in any one of claims 10-13, wherein a source of an ethylene diamine of the general formula $R_2R_3N\text{-}CH_2\text{-}CH_2\text{-}NR_4R_5$, wherein each of R_2, R_3, R_4 and R_5 represents a methyl or ethyl

group is used as organic template R, preferably wherein N,N,N',N'-tetramethyl ethylene diamine is used as organic template R.

15. Process as claimed in any one of claims 10-14, wherein the organic template R is removed substantially by thermal treatment and/or by wet chemical oxidation reaction means, to obtain crystalline aluminophosphates and related compounds substantially free of organic template R.

16. Use of crystalline aluminophosphates and related compounds, as claimed in any one of claims 1-9, in processes involving catalytic reactions, and/or as molecular sieves in separation processes.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3236

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-5 013 535 (BEDART & AL.) * column 3, line 16 - column 4, line 30 * * column 5, line 34 - column 7, line 25 * * examples 1-3 *	1,2,16	C01B25/36 C01B25/45 C01B33/34 B01J29/04
A	EP-A-0 380 825 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) * claims 6-12 * * page 3, line 31 - line 53 * * examples 1-3 *	10-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04 DECEMBER 1992	RIGONDAUD B.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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